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基于新型氨基硫醇单体的高选择性 Hg（II）印记聚合物的合成、表征和分析应用

Synthesis, Characterization and Analytical Application of a High Selective Hg(II)-Imprinted Polymer Prepared from a Novel Aminothiol Monomer

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Abstract

Molecular imprinting is a technique for producing the special polymers which are able to adsorb a special molecule or ion selectively. These polymers create the recognition sites in a macromolecular matrix via imprinting by using a molecular or ionic template. The size and three dimensional image of template and alignment of the functional groups to interact with the target are memorized in the macromolecular matrix after removing the target molecule. The complexation, copolymerization and removing the template after polymerization are the main steps for preparation of ion imprinted polymers (IIPs). The right selection of functional monomer which has high affinity to the ion template is important and effects directly on selectivity.

Since the mercury shows very high affinity to sulfur, the functional monomers containing the sulfhydryl group can produce good stable complex with mercury.

The objective of this thesis is the preparation of a novel high selective Hg(II)-imprinted polymer from 2-Mecaptoethyl amine (MEA) and study on its characterization and analytical application. Since the planned ligand monomer for complexing the mercury ion was novel and not commercially available, it had to be first synthesized in the laboratory. MEA is the simplest stable aminothiol and has NH_2 and SH functional groups in its two ends, which was used for synthesis of a novel polymerizable ligand as called N-methacryloyl-2-mercapto ethylamine (MMEA) by methacryloylating the amino group. Then MMEA was used for complexing the Hg(II) ion via the formation Hg-S bonding. The synthesized complex monomer was applied for preparing a polymer by radical copolymerization with methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) and AIBN as the functional monomer, cross-linker and initiator respectively in the presence of a binary porogen of DMSO and toluene. An Hg(II)-imprinted polymer was obtained after removing the mercury ion from the prepared copolymer that presented a good adsorption capacity and selectivity for mercury in comparison with some competitor ions such as Cd(II) and Zn(II) and CH_3HgCl and with non-imprinted polymer. The Hg-imprinted polymer was also successfully applied for determination of Hg(II) ions in some complex matrices such as tap water and sea water samples.

Abstract

The structure of this thesis contains a general introduction on molecular imprinting and issues relevant to the research in chapter 1. Chapter 2 reports the experimental processes about the synthesis of N-methacryloyl-2-mercapto ethylamine monomer (MMEA) and then Hg(II)–N-methacryloyl-2-mercaptoethyl amine complex monomer (Hg(II)-MMEA) and also the preparation method of Hg(II)-imprinted copolymer. This chapter also contains the spectroscopic data of the synthesized materials and some discussion about the obtained results. The characterization results of the prepared Hg(II)-imprinted copolymer in related to adsorption capacity, pH and kinetics of adsorption and selectivity parameters are presented and discussed in chapter 3. Chapter 4 describes the analytical application of the prepared Hg(II)-imprinted copolymer in matrices of tab water and sea water samples. Chapter 5 describes the other experiments and studies performed in this thesis contain complexing the methylmercury, Preparation of SPME fibers and thermal stability of the prepared Hg(II)-Imprinted copolymer. Chapter 6 summarizes the conclusions from the thesis, as well as the comments for future perspectives. IR and RAMAN spectra are included in the appendix.

Keywords: Molecular Imprinting; Mercury Ion; 2-Mercaptoethyl Amine; N-methacryloyl-2-mercaptoethyl amine; Hg(II)-Imprinted Polymer; SPME; Thermal stability

厦门大学

Abstract in Chinese (摘要)

基于新型氨基硫醇单体的高选择性 Hg（II）印记聚合物的合成、表征和分析应用

分子印迹是通过制备对特定目标分子或离子即模板分子（印迹分子）具有特异预定选择性的聚合物来选择性吸附/富集目标分子或离子的技术。此聚合物通过印迹模板分子或离子在高分子基质中创造识别位点。除去模板分子后，模板分子的尺寸、立体结构和与模板分子相互作用的功能基团空间位置保留于高分子基质中。络合、共聚和聚合后移除模板分子是制作离子印迹共聚物的主要步骤。正确选择对模板离子具有高亲和性的功能单体非常重要，直接影响其选择性。

由于汞表现出对硫具有非常高的亲和力，因此含巯基的功能单体与汞能够产生具有良好稳定性的复合物。

本论文的目的是采用 2-巯基乙胺（MEA）合成对 Hg(II)具有高亲合性的新印迹聚合物，并对其进行表征和分析应用的研究。新研究的与汞离子络合的配位单体无市售，第一次在本实验室合成。MEA 是最简单稳定的氨基硫醇化合物，功能基团 NH_2 和 SH 在其两端。MEA 通过氨基基团的甲基丙烯酸化合成新聚合物配体 N-甲基丙烯酰基-2-巯基乙胺(MMEA)。MMEA 通过形成 Hg-S 键用于络合 Hg(II)。合成的复杂单基体通过自由基共聚合作用合成聚合物，甲基丙烯酸(MAA)、乙二醇二甲基丙烯酸酯(EDMA)和 AIBN 在致孔剂 DMSO 和苯存在条件下分别作为功能单体、交联剂和引发剂。在从合成的共聚物中移除 Hg(II)后所得的印迹聚合物对 Hg(II)相比较其他的竞争离子如 Cd(II)、Zn(II)、CH_3HgCl 和非印迹的聚合物等展现了很好的吸附容量和选择性。Hg 印迹的聚合物也用于测定复杂基质如自来水和海水中的 Hg(II)。

第一章综述了关于分子印迹和与研究相关的一些问题。第二章报告了有关 N-甲基丙烯酰基-2-巯基乙胺单基体（MMEA）和 Hg(II)-N-甲基丙烯酰基-2-巯基乙胺复合单基体(Hg(II)-MMEA)的实验合成过程及 Hg(II)印迹聚合物的制作方法。此章也包括合成材料的光谱数据和对所得结果的讨论。第三章描述制得的 Hg(II)印迹共

聚物在吸附容量，pH 值和动力学吸附和选择性参数的特性，并进行讨论。第四章对 Hg(II)印迹共聚物在自来水和海水基质中的应用进行了叙述。第五章论述了本课题中其他的一些实验研究包括络合甲基汞、制备固相微萃取纤维和制备热稳定的 Hg(II)印迹共聚物。第六章总结了本论文的研究工作，并对将来进一步的研究工作进行了展望。红外光谱和拉曼光谱数据包含在附录中。

关键词

分子印迹；汞离子；2-巯基乙胺；N-甲基丙烯酰基-2-巯基乙胺；Hg(II)印迹聚合物；固相微萃取

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I dedicate this thesis to my wife for her love, encouragement and endurance during the entire period of my Ph.D. program. I also dedicate this thesis to my lovely daughter and son Zahra and Mahdi who are my hopes for future.

I have a special dedication for my parents whose prayings always give confidence and hope to my heart.

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Abbreviations

ABDV	Azo N,N'-bis-divaleronitrile
AFS	Atomic Fluorescence Spectrometer
AIBN	2, 2' AzoIsobutyronitrile
DAAB	Diazoaminobenzene
DMSO	Dimethyl Sulfoxide
DVB	Divinyl Benzene
EDMA	Ethylenglycol Dimethacrylate
EGDMA	See EDMA
FTIR	Fourier Transform Infrared Spectrometer
GC	Gas Chromatography
HCl	Hydrochloric acid
HPLC	High-performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
IIP	Ion Imprinted Polymer
kJ/mol	kili-Joule per mole
MAA	Methacrylic Acid
MEA	2-Mecaptoethyl amine
μg/L	micro gram per liter
mg	miligram
MIP	Molecular Imprinted Polymer
MMEA	N-methacryloyl-2-mercapto ethylamine
ppb	part per billion
ppm	part per million
PVP	Poly Vinyl Pyridine